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TECHNOLOGY NEWS AND TRENDS

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Thermal Technology Tested for Contaminant Recovery

A research project on steam enhanced remediation (SER) for the recovery of dense non-aqueous phase liquid (DNAPL) from fractured limestone has been undertaken at the former Loring Air Force Base Quarry site in Limestone, ME. Participants in the project include the Maine Department of Environmental Protection, U.S. EPA/Region 1, U.S. EPA/National Risk Management Research Laboratory (NRMRL), and the Air Force Base Conversion Agency. The purpose of the research project is to determine if steam injection can be used to enhance the recovery of contaminants from fractured limestone.

A former quarry used for the disposal of more than 400 drums of spent solvents was selected for this research. The fractured rock system at the quarry is highly complex with three sets of fractures and several faults in or around the target area. While tetrachloroethene (PCE) is the main contaminant of concern, other solvents and fuel components also are present. Rock chip samples were extracted with methanol and analyzed by EPA Method 8260 to determine the contaminant distribution. The analytical results showed concentrations up to 100 mg/kg in fractures ranging from 10 to 100 feet below ground surface (bgs). Transmissivity testing done on 10-foot intervals showed that the area generally has very low permeability, ranging from 10^{-4} to less than 10^{-7} m^2/sec. Interconnectivity testing showed that there is limited fracture connectivity between the eastern, middle, and western parts of the site.

Based on the characterization information obtained during the first part of the project, three boreholes forming a semicircle with a diameter of approximately 40 feet at the eastern side of the site were chosen for steam injection. Ten boreholes through the center of the system and in the western side of the site were used for extraction, producing an extraction system approximately 60 feet wide and 150 feet long. A system of 23 thermocouple wells and electrical resistance tomography (ERT) implemented from nine boreholes was used to monitor temperature and steam flow. The sparsely fractured, low-transmissivity nature of the site limited the amount of steam that could be injected; thus, three extraction wells that were not producing significant amounts of contaminants were converted to steam injection wells after 30 days of injection. Operational techniques such as injection pressures, air injection, and drawdown of ground-water levels to create pressure cycling were tested to determine their effects on injection and extraction rates. The total period of the injection was limited by the budget to 83 days followed by 7 days of extraction.

Daily effluent samples of both the vapor and aqueous phases showed that extraction rates initially were low and generally decreased during the first three weeks of the demonstration, much as would be expected during conventional pump and treat operation. Subsurface temperature and ERT monitoring indicated that the steam and hot water condensate followed rather narrow paths in the limestone, and that only a small fraction of the rock was heated to steam temperature. Even these small temperature increases, however, significantly increased the effluent

[continued on page 2]

Contents

RevTech Conference Coming in July

The U.S. EPA's Technology Innovation Office (TIO) is sponsoring a new conference that showcases smart assessment and cleanup strategies involved in site reuse and land revitalization programs. The *RevTech* conference will be held July 22-24, 2003, at the Pittsburgh Marriott City Center. Online registration and additional information is available at http://brownfieldstsc.org.

[continued from page 1]

concentrations in both the vapor and aqueous phases. Aqueous concentrations of gasoline range organics, diesel range organics, and volatile organic compounds (VOCs) increased by an order of magnitude and more during the demonstration. Vapor phase concentrations increased slowly while steam was injected, and concentrations jumped by more than an order of magnitude when the pressure in the subsurface decreased as steam injection ended. At the time the demonstration ended, effluent concentrations were continuing to increase.

Post-treatment sampling of ground water and rock chips from within the treatment area will be used to determine remaining contaminant levels. Ground-water samples from two angled boreholes that begin next to the treatment area and extend below it will be used to determine if contaminants were mobilized downward or horizontally. Although remediation was not taken to completion, the observed steam flow and removal mechanisms suggest that SER can more effectively increase the mass removal rate than traditional methods such as pump and treat or soil vapor extraction.

Contributed by Eva Davis, U.S. EPA/ORD (580-436-8548 or davis.eva@epa.gov)

Searching Made Easier for Perchlorate Remediation Resources

TIO is compiling information on research and application of technologies used for cleaning up perchlorate-contaminated ground water. As part of its effort to advocate more effective, less costly approaches to site cleanups, TIO has made this information available through a single location on its CLU-IN web site at http://cluin.org/perchlorate. The compilation currently includes policy and guidance documentation, related web links, technical presentations, and over 30 studies and reports on perchlorate issues.

SERDP and NRMRL Sponsor Field Test of Cosolvent-Enhanced DNAPL Removal

In July 2001, Clemson University and the U.S. EPA/NRMRL field tested cosolvent flooding for in-situ remediation of DNAPL source zones. The test was conducted at the Dover National Test Site (DNTS) at Dover Air Force Base, DE, as part of an enhanced source removal demonstration project funded by NRMRL and the Strategic Environmental Research and Demonstration Program (SERDP). Final test results estimated an 80% reduction in contaminant mass after 37 days of treatment.

The cosolvent flood test was performed in a 15-by-10-foot watertight cell lined by sheet-pile walls extending 45 feet bgs. The cell contained twelve 2-inch wells with 20-foot slotted screens and a 3-dimensional network of 108 small fluid samplers positioned at discrete vertical intervals below the water table, which was at 29 feet bgs. Site geology consists of unconsolidated Atlantic Coastal Plain sediments with interbedded sands, silts, and clays, and an average hydraulic conductivity of about 1×10^{-3} cm/sec.

Previous field testing of air sparging in this cell involved a controlled release of 66 liters (106.9 kg) of pure PCE. Air sparging removed approximately 58 liters (94.0 kg) of PCE, leaving a PCE residual of approximately 8 liters (13.0 kg). Prior to the flood test, an additional 48.9 liters (79.2 kg) of PCE were released to reach a total volume of 57 liters (92.3 kg). The PCE was released at a depth of 35 feet, producing a treatment zone extending from 35 feet bgs to the confining clay layer at 40 feet bgs.

The cosolvent flood consisted of a mixture of 70% *n*-propanol and 30% saltwater. Prior to mixing, a concentrated saltwater solution was prepared by adding 175 grams of food-grade calcium chloride dihydrate to each liter of water used in the mixture. Saltwater was selected as a component due to its very high density in comparison to water or propanol, and its associated capability to improve cosolvent delivery to lower parts of the aquifer. Saltwater also increased the partitioning of propanol into PCE, thereby decreasing density of the DNAPL and reducing its potential for downward mobilization during the flooding.

An initial non-reactive tracer test performed after the release revealed a distinct and isolated high permeability zone near the upper part of the saturated zone, which marginally reduced efficiency of the cosolvent flooding process. Ground-water samples collected from the extraction wells during the tracer test contained consistently high levels of dissolved PCE, with an average concentration of approximately 80 mg/L. The individual multilevel samplers had highly variable dissolved PCE concentrations, ranging from nearly zero to the point of PCE's aqueous solubility (about 160 mg/L).

Cosolvent flooding operated for a total of 37 days, at an average flow rate of 3.2 liters per minute. The cosolvent solution was recycled through air stripping and then reinjected. The flood used a total of 33,000 liters of 70% *n*-propanol and 30% water. Due to treatment and re-injection, 80,000 liters of remedial fluid were displaced through the test cell. Maximum PCE concentrations in the extraction wells ranged from 1,000 to 1,500 mg/L, or nearly ten times the normal aqueous solubility. No DNAPL or LNAPL was produced from the extraction wells.

Over the course of field testing, a total of 73.5 kg of PCE was extracted from the test cell (Figure 1). Post-treatment ground-water sampling of the extraction wells showed

[continued on page 3]

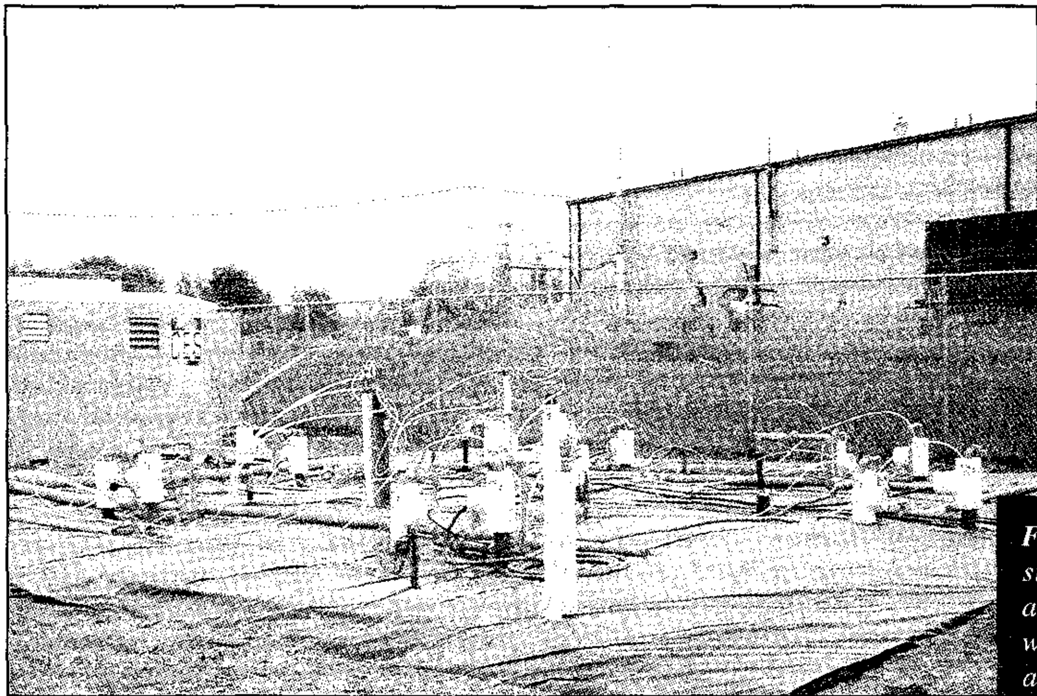

Figure 3. Six-phase subsurface heating at the Silresim site was applied through a hexagonal array of 14 electrodes.

[continued from page 4]

in the wells of each shallow electrode and connected to the vapor extraction system to "slurp" water and maintain a constant water level. In addition, electrolyte drip lines were installed in the filter pack to maintain adequate moisture for electrical conduction. Power was delivered to each deep electrode through a parallel connection from its paired shallow electrode. The shallow electrodes drew approximately 20 amps of current, while the deep ones drew approximately 250 amps.

The vapor collection system consisted of 4-inch CPVC headers with 1¼-inch, high-temperature, chemical-resistant hose connections to each electrode. Emitted vapor was directed sequentially to an air-water separator, a plate-and-frame heat exchanger/condenser, a cyclone separator, three 8,000-lb vapor-phase carbon vessels in series, and a regenerative vacuum blower. The total vapor flow rate was approximately 300 scfm; of this, approximately 70% was attributed to the horizontal collection pipes located near the perimeter of the hexagon, 20% to the shallow electrodes, and 10% to the deep electrodes (as a pressure relief for the saturated zone). Treated vapors were discharged through a 15-ft stack. A total of approximately 48,000 pounds of granular activated carbon was used for vapor treatment during the pilot project.

Four thermocouple strings were installed inside and immediately outside the electrode array; the interior strings were placed equidistant from the electrodes, where heating was least effective. The thermocouples (nine per string) were installed at 5-ft intervals to a depth of 45 feet. Ground temperatures reached steam temperatures at a depth of approximately 40 feet, and increased to 115°C at 35 feet. After eight weeks of heating, temperatures in the target interval for the subsurface treatment zone achieved boiling temperatures. Measurements of ambient vapor concentrations using field instruments indicated no uncontrolled vapor emission from the electrode array throughout the pilot test operations.

Overall, soil conducted electricity at levels higher than anticipated, possibly due to the presence of buried metal waste. Minor stray electrical voltages were observed outside the

[continued on page 6]

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Ann Eleanor
Technology Innovation Office
(5102G)
U.S. Environmental Protection Agency
Ariel Rios Building
1200 Pennsylvania Ave, NW
Washington, DC 20460
Phone: 703-603-7199
Fax: 703-603-9135

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[continued from page 5]

electrode array during system startup. Placing a chain-link mesh outside the array and grounding it to a distant monitoring well remedied this problem. In addition a pre-pilot resistivity survey would have helped to assess the potential for undesired stray voltage during treatment.

A significant setback was encountered during the second month of operation when cracks in the CPVC piping (leading from the electrodes to the vapor header) resulted in an atmospheric release of steam and vapor. Operations were shut down for several days but resumed after the degraded CPVC was replaced with flexible chemical-resistant hose. This unexpected condition appeared to result from a combination of excessive heat, pressure, and chemical attack from a variety of contaminants.

Post-test analysis showed that shallow ground-water contamination (<24 feet bgs) in the treatment zone decreased more than 99%, and deeper ground-water contamination (24-40 feet bgs) decreased more than 76%. Analytical results also indicated a 95% reduction in contaminated soil mass.

Additional analysis of the pilot results will determine whether ERH technology could be used to achieve project cleanup goals that were not met through 1997-1998 implementation of a soil vapor extraction (SVE) system. Although SVE treatment resulted in the removal of approximately 12 tons of subsurface VOCs over a 14-month period, concentrations in the vadose and saturated zones remained significantly higher than their maximun contaminant levels. Results of the ERH pilot suggest that this technology can increase mass removal efficiencies in both the vadose and saturated zones more effectivaly than traditional SVE.

The ERH pilot cost approximately $1.6 million, including $50,000 for electrical power and $50,000 for vapor treatment. Modeling based on total VOC concentrations exceeding 10 mg/kg indicates that 1.02 million tons of soil require additional treatment.

Contributed by Sharon Hayes, U.S. EPA/Region 1 (617-918-1328 or hayes.sharon@epa.gov) and John Scaramuzzo, Tetra Tech FW, Inc. (617-457-8297 or jscaramuzzo@ttfwi.com)

ERRATA

In the March 2003 *Technology News and Trends* article, "DNAPL Treatment Demonstration Completed at Cape Canaveral," the contributors believe use of the terms "treatment efficiencies" and "cleanup efficiencies" may be misleading due to uncertainties in mass removal estimates for the SPH demonstration. The appropriate language is "apparent mass reduction." The SPH cost of "$164" for each kg of TCE removed or destroyed should read "$64."